



Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: The EUSAAR protocol

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Institute for Environment and Sustainability



EUR 23441 EN - 2008

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JRC 46588

EUR 23441 EN
ISBN 978-92-79-09561-0
ISSN 1018-5593
DOI 10.2788/87062

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Cover: After A. Pozzi "Uomo e nuvola nera"
Printed in Italy

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Abstract

Thermal-optical analysis is a conventional method for classifying carbonaceous aerosols as organic carbon and elemental carbon. Unfortunately, different thermal evolution protocols result in a wide elemental carbon-to-total carbon variation up to a factor of five. In Europe, there is currently no standard procedure for determining carbonaceous aerosol fraction which implies that data from different laboratories at various sites are most likely not comparable and affected by unknown errors. In the framework of the European project EUSAAR (European Supersites for Atmospheric Aerosol Research), a comprehensive work has been carried out to investigate the causes of differences in the EC measured using different thermal evolution protocols and attempts have been devoted to assess and mitigate major positive and negative biases affecting thermal-optical analysis. Our approach to improve the accuracy of the thermal-optical discrimination between organic carbon and elemental carbon was essentially based on four goals. First, as charring correction relies on assumptions proven to be generally not true –e.g. pyrolic carbon is considered to evolve completely before native elemental carbon throughout the analysis–, we sought to reduce pyrolysis to minimum levels in favour of a maximum volatilisation of organic carbon. Second, we sought to minimize the potential negative bias in EC determination caused by early release of light-absorbing species at high temperature in the He-mode, including native EC or a combination of EC and pyrolytic carbon with potentially different specific cross section values. Third, we sought to minimize the potential positive bias in EC determination resulting from the slipping of residual organic carbon into the He/O₂-mode and its potential evolution after the split point. Finally, we sought to reduce the uncertainty arising from the position of the OC/EC split point on the FID profile through multiple desorption steps in the He/O₂-mode. Based on different types of carbonaceous PM encountered across Europe, we defined an optimised thermal evolution protocol, the EUSAAR_2 protocol, as follows: step 1 in He, 200 °C for 120 s; step 2 in He 300°C for 150s; step 3 in He 450°C for 180s; step 4 in He 650°C for 180s. For steps 1-4 in He/O₂, the conditions are 500°C for 120s, 550°C for 120s, 700°C for 70s, and 850°C for 80s, respectively.

1 INTRODUCTION

Atmospheric elemental carbon (EC) is a ubiquitous component of particulate matter in the fine fraction and appears at measurable levels in even the most remote locations (Goldberg, 1985). It has been observed that EC comprises from 8 to 17% of the atmospheric fine aerosol mass concentration at European rural and urban background sites and kerbside sites, respectively (Putaud et al., 2004). EC is a persistent product of incomplete combustion, principally of combustion of fossil fuels in transportation, heating, power generation, and industrial processes, wood for residential heating, and agriculture. The prevalence of aerosol EC has been a concern because of its suspected adverse effects on health (Highwood and Kinnarsley, 2006; Bérubé et al., 2007; Adar and Kaufman, 2007). In recent years, scientific attention has also been given to its role as a driver of global warming (e.g. Jacobson, 2001; Ramanathan and Carmichael, 2008).

Measurement of atmospheric EC has long been problematic, largely due to the fact that its chemical, physical, and morphological nature is complex and quite variable. Among other methods, a variety of thermal and thermal-optical measurement techniques have been developed to measure organic carbon (OC) and EC. While these methods generally measure the same amount of total carbon (TC), the discrimination between OC and EC is operationally defined with large differences in the amount of OC and EC measured by different methods (e.g. Schmid et al., 2001; ten Brink et al., 2004).

The present work mainly focuses on thermal-optical technique. In thermal-optical analysis (TOA), the carbonaceous material in aerosol particles deposited on a quartz-fiber filter is thermally desorbed according to prescribed temperature protocols, first in an inert atmosphere and then in an oxidizing atmosphere. A continuous gas stream carries the desorbed carbonaceous material through an oxidizer (typically a tube containing MnO_2 at 870°C or 912°C), which efficiently converts carbon-containing molecules in CO_2 . CO_2 can be detected directly, e.g. by nondispersive infrared spectroscopy, or indirectly, by reduction to CH_4 followed by flame ionization detection. Ideally, organic carbon would desorb in the inert gas stream such as Helium, while EC combusts in the oxidizing atmosphere – typically O_2 in He – at high temperature. A complicating factor is that some thermally unstable organic compounds pyrolyse in the He-mode of the analysis and char on the filter to form pyrolytic carbon (PC) and usually require an oxidizing atmosphere to evolve off the filter, like native EC. Not accounting for PC formation can very significantly bias the discrimination between OC and EC (e.g. Schmid et al. 2001; Schauer et al. 2003). To correct for pyrolysis, the light transmission (TOT) through the sample is monitored before and during the analysis with a red laser beam. As PC absorbs the laser light, transmission decreases while organic matter chars in the He-mode. When the charred organic carbon PC, and EC are released from the filter in the He/ O_2 -mode, transmission increases, and the point at which the transmission reaches its initial value (pre-pyrolysis) is used to discriminate OC and EC (OC/EC split). An alternative to this approach is the thermal-optical reflectance (TOR) method which uses the reflected laser light to determine the OC/EC split (Chow et al. 1993). The IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol (Chow et al., 1993) and the NIOSH (National Institute of Occupational Safety and Health) protocol (Birch and Cary, 1996) are the most widely thermal-optical protocols used in the atmospheric science community. Traditionally, the IMPROVE protocol is applied to

samples from non-urban background site in US IMPROVE network, while the NIOSH one is applied to samples from urban sites in USA-EPA's Speciation Trends Network (STN). These protocols differ in temperature set points – higher for NIOSH (e.g. the highest temperature in He is 850°C) than for IMPROVE (e.g. the highest temperature in He is 550°C) analysis– and for residence times at each temperature step –typically longer for IMPROVE than for NIOSH analysis. Moreover, the IMPROVE protocol uses the reflectance method to correct for charring, while the NIOSH protocol has adopted the transmittance method. Previous studies have demonstrated that such differences in the thermal-optical evolution and charring correction might significantly alter the measured amounts of OC and EC by a factor of five (e.g. Chow et al., 2001, Conny et al., 2003, Chow et al., 2004).

In Europe, there is currently no standard procedure for analysing the carbonaceous aerosol fraction, which implies that data from different laboratories at various sites are most likely not comparable and affected by unknown errors. The EU-project EUSAAR (EUropean Supersites for Atmospheric Aerosol Research, www.eusaar.net) integrates 20 high quality European ground-based stations with the objective of harmonizing measurements of aerosol properties of interest to air quality and global climate through coordinated protocols. Within this framework, efforts have been devoted to investigate the causes of differences in the EC measured using different thermal evolution protocols and attempts have been made to assess and then mitigate the major positive and negative biases affecting thermal-optical analyses. The work presented here led to the definition of an optimised thermal-optical protocol, the EUSAAR_2 protocol.

2 METHODS

Samples and analysis

Different types of samples were investigated in this study: i) PM_{2.5} ambient aerosol samples collected on quartz-fiber filters at Ispra, the EMEP - GAW regional station in Northern Italy and at various background sites across Europe; ii) filters spiked with fulvic acid from the Suwannee River (IHSS), a polymeric organic substance with a high degree of aromaticity which can mimic *humic-like-substances* found abundant in the fine atmospheric aerosol (Hoffer et al., 2006); iii) filters spiked with levoglucosan, a major component of wood smoke aerosol; iv) samples of both biogenic and anthropogenic secondary organic aerosol (SOA) generated in a smog chamber from the photo-oxidation of α -pinene and toluene, respectively. These experiments were performed in a 2000 L reaction chamber, equipped with on-line FT-IR (Fourier Transformed Infrared Spectroscopy) to follow the reaction [ca 2 ppmV of the gaseous precursor was mixed with 2-5 ppmV of 2-propyl-nitrite-*d*₆, CD₃CHONOCD₃]. UV-light ($\lambda \geq 300$ nm) was switched on for five hours to produce OH radicals and, thereby, to initiate the photo-oxidation of gaseous precursors. The organic aerosols produced were then collected on quartz-fiber filters and stored below 5°C before analysis. v) Light-absorbing-carbon-only (LAC-only) samples generated by thermal treatment of PM_{2.5} ambient aerosol samples according to the method proposed by Yu and Li (2003), which contain a mixture of pyrolysed organic carbon PC and native EC.

The samples were analysed using a Sunset Laboratory Dual-Optical Carbonaceous Analyser. The carbon analyzer is operated using Ultra-High Purity (Grade 6.0) Helium gas with a moisture/hydrocarbon/oxygen trap installed on the inlet to avoid problems with contaminations. The instrument is calibrated prior to use with a sucrose standard and manual CO₂ injections. The calculation procedures for defining the OC/EC split uses the algorithm as described by Sunset Labs (David Smith, personal communication, 2006). Carbon evolving after the laser (678 nm) signal reaches approximately 97% of the initial pre-pyrolysis value, (the initial pre-pyrolysis value is an average of the laser signal over 30s before the start of the analysis), is classified as native EC. In general, a value of 97% takes into account the temperature inherent bias in the laser signal, according to the Sunset Labs data analysis program.

Table 1 lists the NIOSH, the IMPROVE, the EUSAAR_1 long and the EUSAAR_1 short protocols; furthermore, to the different purposes of the experiments performed in this study, the EUSAAR_1 long protocol has been *modified* varying the temperature of the last step in the He-mode to 550°C, 750°C and 850°C. We refer to these protocols as He4-550, He4-750 and He4-850, respectively. These protocols are based on the temperature measured by a thermocouple located ca. 20 mm downstream of the sample which may be not exactly equal to the sample temperature (Chow et al., 2005).

Table 1 Temperature protocols used to analyse samples in the present work: temperature set point and residence time are reported.

	NIOSH ^b	IMPROVE ^c	EUSAAR_1 short	EUSAAR_1 long	He-550	He-750	He-850
STEP	T, duration	T, duration	T, duration	T, duration	T, duration	T, duration	T, duration
He1	310°C, 60s	120°C, 150-580s	200°C, 120s	200°C, 180s	200°C, 180s	200°C, 180s	200°C, 180s
He2	475°C, 60s	250°C, 150-580s	300°C, 150s	300°C, 240s	300°C, 240s	300°C, 240s	300°C, 240s
He3	615°C, 60s	450°C, 150-580s	450°C, 180s	450°C, 240s	450°C, 240s	450°C, 240s	450°C, 240s
He4	870°C, 90s	550°C, 150-580s	650°C, 180s	650°C, 240s	550°C, 240s	750°C, 240s	850°C, 240s
(Helium)	Cool down, 45s	–	Cool down, 25s	Cool down, 25s	Cool down, 25s	Cool down, 25s	Cool down, 25s
He/O ₂ 1 ^a	550°C, 60s	550°C, 150-580s	850°C, 150s	550°C, 300s	550°C, 300s	550°C, 300s	550°C, 300s
He/O ₂ 2	650°C, 60s	700°C, 150-580s		850°C, 180s	850°C, 180s	850°C, 180s	850°C, 180s
He/O ₂ 3	700°C, 60s	850°C, 150-580s					
He/O ₂ 4	770°C, 60s						
He/O ₂ 5	870°C, 110s						

^a A mix of 1% oxygen in UHP helium.

^b The temperature program for the NIOSH method is reported in Birch, 1998.

^c The residence time at each temperature in the IMPROVE protocol depends on when the flame ionization detector (FID) signal returns to the baseline to achieve well-defined carbon fractions.

3 RESULTS and DISCUSSION

In thermal-optical analyses, the correct discrimination between OC and EC relies upon one or the other of the following two assumptions: 1) PC is assumed to have the same specific cross section (σ) as atmospheric native EC. If so, regardless of when PC and EC actually come off the filter during the analysis, desorbed carbon amount beyond the split point is equivalent to the mass of the native EC on the filter. 2) Alternatively, PC is considered to evolve completely before native EC throughout the analysis; in such case, despite possible differences in the specific cross section of PC and EC, the post split point carbon mass represents the true native EC. Previous studies have however demonstrated that neither of these assumptions always holds. PC and EC are found to co-evolve from the He/O₂-mode and, even prematurely, from the He-mode at high temperatures; moreover, their specific cross section may significantly differ (e.g. Chow et al. 2004, Yang and Yu, 2002; Yu et al., 2002; Subramanian et al., 2006; Han et al., 2007). There might be, therefore, inherent biases in either direction in the determination of OC and EC. Consequently, the thermal-optical protocol was adjusted to mitigate the effects of *events* during the analysis that can potentially even magnify those biases in the OC/EC split. We attempted to satisfy the following optimization criteria:

1- charring is reduced to minimum levels so that possible differences in specific cross section, σ , of PC and EC have a minimum impact on the accuracy of the optical correction and, thus, of the discrimination between OC and EC.

2- evolution and/or pyrolysis of OC is completed at the end of the He-mode to avoid that unevolved and uncharred left-behind OC slip into the He/O₂-mode. This will, in turn, reduce the uncontrolled risk that a fraction of non-light-absorbing organic carbon evolves even after the OC/EC split and positively biases the measured EC value.

3- premature evolution of light-absorbing carbon is limited during the He-mode to prevent that the early released LAC species contains native EC. In such a case the resulting post-split EC might be altered, because of possibly different specific cross section of EC and PC.

4- multiple desorption steps are designed for the He/O₂-mode to ensure that the position of the OC/EC split point occur where the FID response profile is low; the uncertainty in the split point position will result in a minimum uncertainty in the discrimination of OC and EC.

With this in mind, key parameters were investigated in designing the EUSAAR_2 thermal protocol and specifically 1) steps at low temperature; 2) the He-mode maximum temperature; 3) residence time of each temperature step; and 4) temperature steps in He/O₂.

3.1 Temperature set points

3.1.1 Low Temperature Steps in the He-mode

A set of samples has been analysed using a NIOSH thermal protocol (NIOSH 1999) and a *modified* version of this protocol. The two protocols differ essentially for steps at low temperature; in particular the NIOSH protocol has a single step at 310°C of 60 s (**Table 1**) whereas two steps at 200°C and 300°C with a significant longer residence time of 180s and 240s, respectively were implemented in the *modified* version of the NIOSH protocol.

Runs show that the amount of OC evolving up to a temperature of about 300°C is $15.7 \pm 1.3\%$ higher in the *modified*-NIOSH than in the original NIOSH protocol (**Table 2**).

Table 2 TC OC and PC, in $\mu\text{g cm}^{-2}$ units, obtained from analysis of aerosol samples using both a NIOSH thermal protocol (NIOSH 1999) and a version *modified* by the addition of steps at low temperature. OC is reported as the organic carbon peaks, evolved in the He-mode prior to and after 300 °C; PC is estimated by the sample transmittance over the entire He-mode and assuming a specific absorption cross section of $45 \text{ m}^2/\text{gC}$.

THERMAL	sample	TC $\mu\text{g cm}^{-2}$	OC $\mu\text{g cm}^{-2}$		*PC $\mu\text{g cm}^{-2}$
			$\leq 300 \text{ }^\circ\text{C}$	$> 300 \text{ }^\circ\text{C}$	
NIOSH	1	11.59	2.41	4.27	3.87
<i>Modified</i> NIOSH	1	11.51	2.81	4.20	3.36
NIOSH	2	12.79	2.82	4.54	1.99
<i>Modified</i> NIOSH	2	12.79	3.29	4.60	1.67
NIOSH	3	8.33	1.93	3.05	3.62
<i>Modified</i> NIOSH	3	8.30	2.21	2.98	3.12

*PC peak area estimated from the sample transmittance

The two additional steps allow a larger release of organic carbon prior to a more aggressive heating; the OC amount available for evolution and/or pyrolysis at higher temperatures is, then, lower. **Table 2** reports the OC, in $\mu\text{g}/\text{cm}^2$ units of organic carbon peaks, evolved in the He-mode prior to and after 300 °C. Interestingly, the overall amount of pyrolytic carbon formed -estimated by the sample transmittance and assuming a specific absorption cross section of $45 \text{ m}^2/\text{gC}$ (Subramanian et al. 2007)- is larger in the NIOSH protocol than in the *modified* one: on average, PC formation in the *modified* NIOSH protocol is $85.6\% \pm 1.4\%$ of that in the NIOSH method. In

other words, the OC that would have evolved at lower temperatures if given more time contributes to enhance charring at higher temperature steps in the NIOSH method. In agreement with Yu et al. 2002, results indicate that the extent of charring formation is strongly dependent on the temperature set-points employed for analysis and also that prolonging residence times can favor a more complete carbon evolution and, consequently, reduce charring formation. Because of unequal specific cross section values for PC and EC, a reduction of charring formation improves, in turn, the accuracy of the OC/EC split.

Two steps at low temperature, i.e. 200°C and 300°C, with a residence time of 180 s and 240 s, respectively were therefore implemented in He-mode of the EUSAAR_1 long protocol, to allow maximum release of organic carbon prior to a more aggressive heating and the consequent onset of charring.

Furthermore, a set of samples has been analysed using EUSAAR_1 long protocol in presence and absence of oxygen at He1 and He2 steps. In contrast with Cachier et al. (1989) and Ohta and Okita (1984), our results show negligible differences in the amounts of charred carbon when oxygen-containing vs. oxygen-free carrier gas is used for the lowest temperature steps. Therefore, taking into consideration the risk of EC combustion in an oxidizing atmosphere when temperature approaches 340°C, and the potential temperature biases (i.e. deviation from temperature set-points) in e.g. the Sunset Lab. Instrument (Chow et al., 2005), an inert atmosphere was finally selected for the first two steps of the EUSAAR_1 long protocol.

Figure 1 Thermograms from the analysis of a typical ambient PM2.5 sample collected in Ispra, with the (a) NIOSH-type and (b) He-550 protocols

Fig 1a

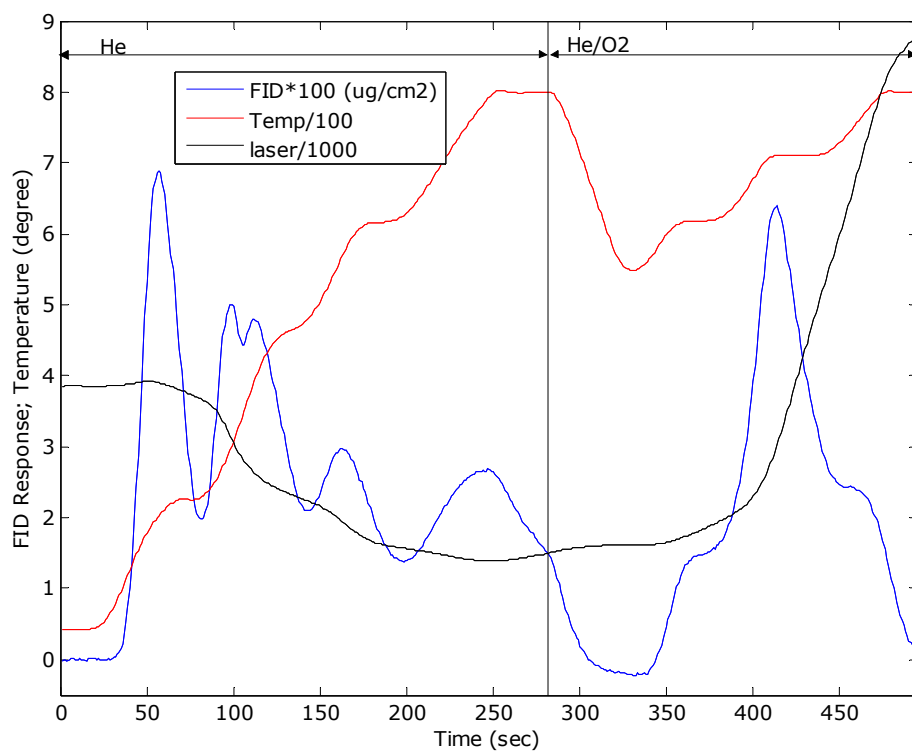
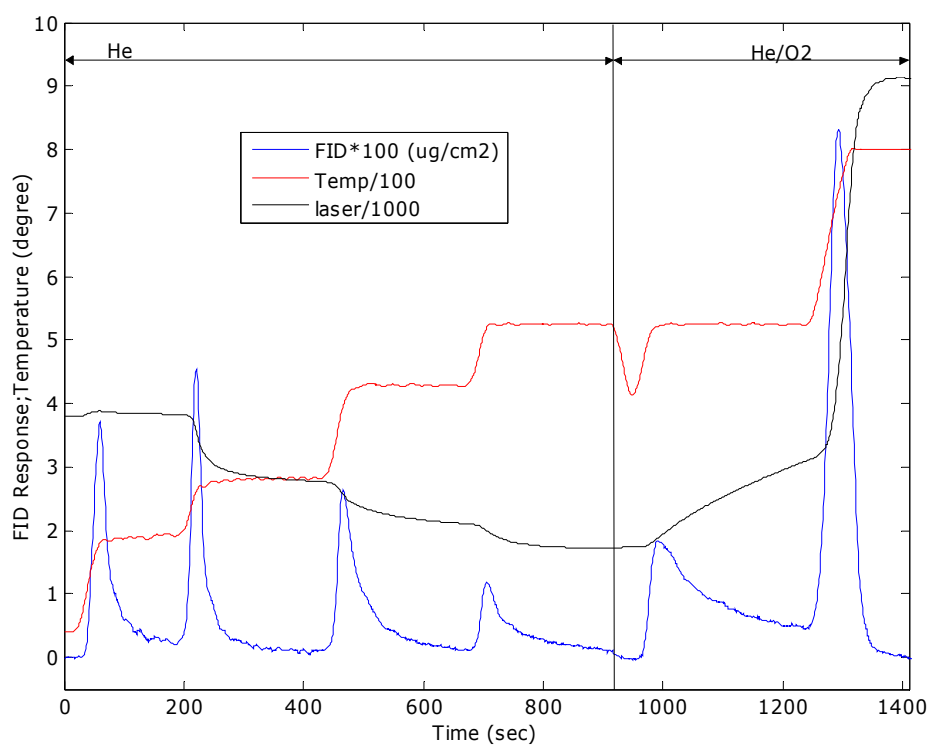


Fig 1b



3.1.2 Maximum He-mode Temperature and Premature LAC evolution

A thermogram obtained from the analysis of a PM_{2.5} aerosol sample collected in Ispra using a NIOSH-type thermal protocol (Birch, 1998) is shown in **Figure 1a**. The formation of light-absorbing pyrolysed carbon (PC) causes the transmission of laser light through the sample to decrease through much of the He-mode of the analysis. The transmission reaches a minimum value partway through the 850°C temperature step of the He-mode and then begins increasing, indicating the premature evolution of light-absorbing carbon (LAC). The loss of light-absorbing carbon at high temperature in the He-mode of the analysis is not specific of Ispra samples: many examples are reported in the literature (e.g. Chow 2001; Subramanian et al. 2006). At high temperatures, mineral oxides that are part of the filter deposit can supply oxygen indeed promoting combustion of LAC in an inert environment. Some light-absorbing heavy tar-like organics (similar to PC), often present in wood smoke sample, may also evolve (Fung 1990).

In the event of a loss of light-absorbing carbon in the He-mode of the analysis, the critical issue is to determine the type of this light-absorbing carbon that evolves. Yu et al. (2002) suggest that it is PC. More recently, Subramanian et al. (2006) demonstrated that the light-absorbing carbon evolving in the He-mode can be either native EC or PC or a combination of them. If the LAC evolving in the He-mode at high temperature is pure pyrolysed organic carbon this does not produce any bias in OC and EC determination. On the other hand, the premature evolution of EC or of a combination of PC and EC might also be accounted for by the laser response in the He/O₂-mode (so that the mass of post-split carbon represents the mass of native EC), but only if PC and EC have the same specific cross section. However, pyrolytic carbon has been reported to have generally higher specific cross section values than native EC (Chow et al., 2004; Subramanian et al., 2006). Indeed, literature values of specific cross section for EC deposited on quartz filters, σ_{EC} , range from 8.1 m²/g-C to 25.4 m²/g-C for solvent-extracted ambient samples (Gundel et al., 1984; Lioussé et al., 1993; Petzold et al. 1997; Subramanian et al., 2006). The large variability in σ_{EC} depends on various factors as aerosol aging, the extraction/thermal method employed and the filter substrate. Similarly, it is expectable that the σ value of PC is largely affected by the composition of its organic precursors, which vary greatly among aerosol collected from different locations and at different times, and by the thermal evolution protocol applied for the analysis. Nevertheless, values reported in the literature for PC specific cross section are almost always greater than 25 m²/gC. In particular, 35 m²/gC is found for Pittsburgh samples (Subramanian et al., 2006), 52.8 ± 10.6 m²/gC for Fresno samples and 48.5 ± 3.9 m²/gC is reported for IMPROVE network samples (Chow et al., 2004). Under these circumstances, premature evolution of light-absorbing carbon (i.e. EC or a combination of PC and EC) in the He-mode would cause the EC defined by a He4-850 protocol, as NIOSH (**Figure 1a**), to underestimate the native EC, as compared to the EC obtained by protocols with no occurrence of early LAC loss. In summary, since we cannot exclude that 1) the LAC species evolving in the He-mode at high temperature is EC or a combination of PC and EC and 2) the specific cross section of PC and EC differ largely, it becomes essential to limit, as far as possible, the release of LAC during the He-mode, which could otherwise be counted as OC. A solution is to lower the maximum temperature of this mode. **Figure 1b** shows the thermogram from the He-550 analytical protocol (**Table 1**) of the same sample as in **Figure 1a**.

Figure 2 Thermograms from the analysis of light-absorbing-carbon-only samples with the EUSAAR_1 (a), He-750 (b) and He-850 (c) protocols. The LAC-only samples were generated, as a mixture of pyrolysed organic carbon and native EC, by thermal treatment of PM2.5 ambient aerosol samples according to the method proposed by Yu and Li (2003).

Fig 2a

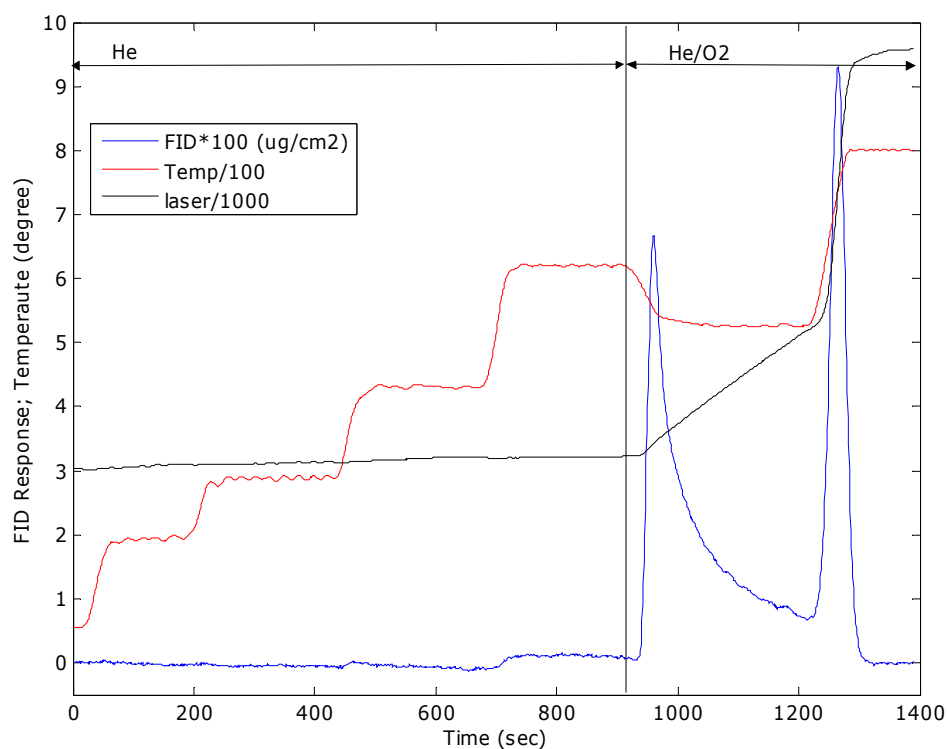


Fig 2b

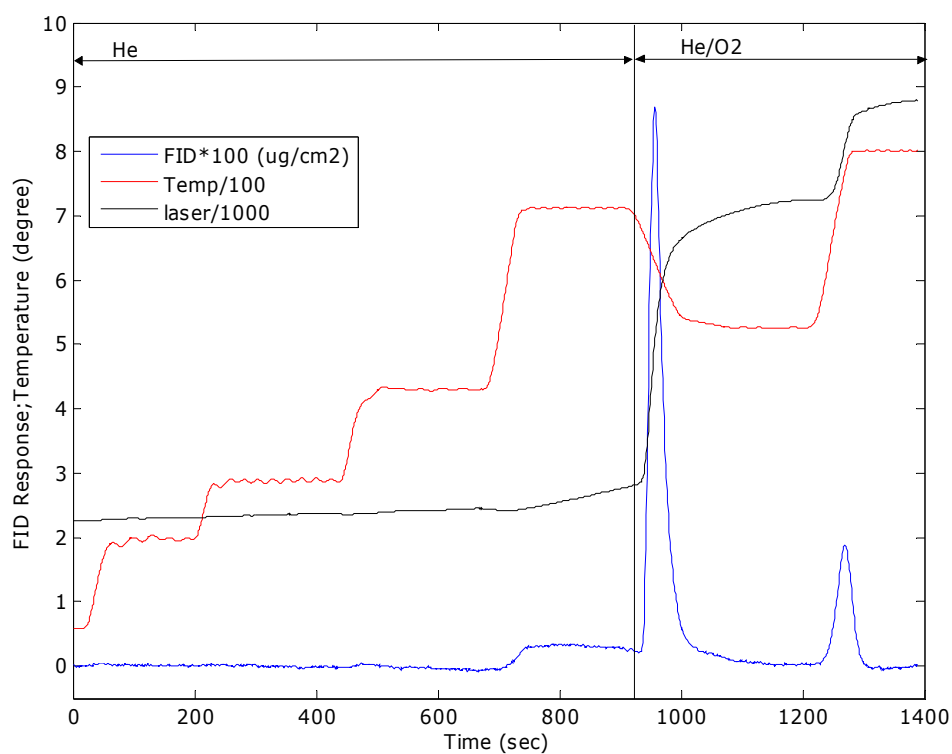
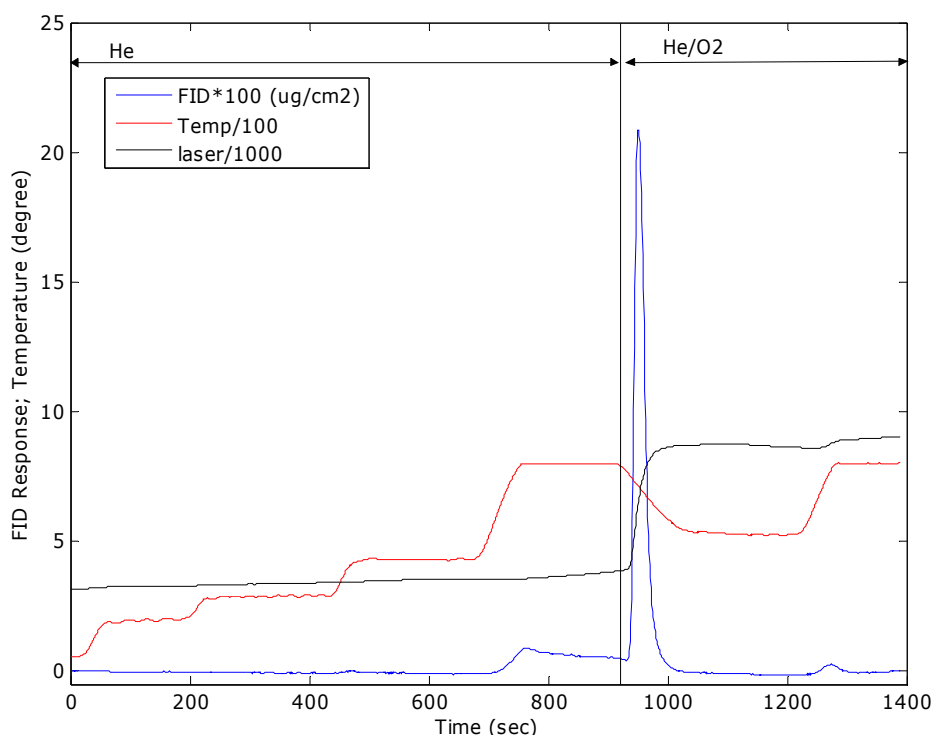


Fig 2c

The laser signal reaches its minimum value in the He₄ step (550°C) and does not increase until the He/O₂-mode, suggesting no loss of light-absorbing carbon in the He-mode. It should be noted, however, that a constant transmission signal in the He₄ step, as observed in the He-550 analysis, does not totally exclude that LAC is lost in the He-mode since LAC release might be perfectly balanced by on-going pyrolysis (**Figure 1b**).

On top of this, thermal-optical analyses of light-absorbing-carbon-only samples were performed to identify the temperature at which premature evolution of LAC starts and to assess the extent of this bias. LAC-only samples were generated by thermal treatment of PM_{2.5} ambient aerosol samples according to the method proposed by Yu and Li (2003), leading to a mixture of PC and native EC. **Figures 2** shows thermograms of LAC-only samples analysed with EUSAAR₁ long (max temperature in He 650°C, **Figure. 2a**), He-750 (**Figure 2b**) and He-850 (**Figure 2c**) protocols. For the analysed samples, an increase of the maximum He-mode temperature causes an increase in the fraction of LAC evolving in that temperature step. On average $2.5 \pm 2.4\%$, $16.2 \pm 5.9\%$ and $21.2 \pm 4.4\%$ of the total LAC (note that LAC equals TC in this experiment) is found to prematurely evolve in He at 650°C, 750°C and 850°C, respectively. These observations imply that the amount of EC measured in the original PM_{2.5} ambient aerosol samples using EUSAAR₁ long, He-750 and He-850 protocols could be biased by extents which are progressively larger as the maximum He-mode temperature increases. Moreover, potential biases produced by a protocol with the maximum temperature in the He-mode of 650°C (as the EUSAAR₁ protocol) appear quite moderate, if not negligible.

Figure 3 Thermograms from the analysis of toluene photo-oxidation aerosol products (a), α -pinene photo-oxidation aerosol products (b), levoglucosan (c) and fulvic acid (d). The protocol used for the analysis is an *modification* of the EUSAAR_1 protocol in which steps He-4 at 550°C, He-6 at 750°C and He-7 at 850°C are added, each of 240 s.

Fig 3a

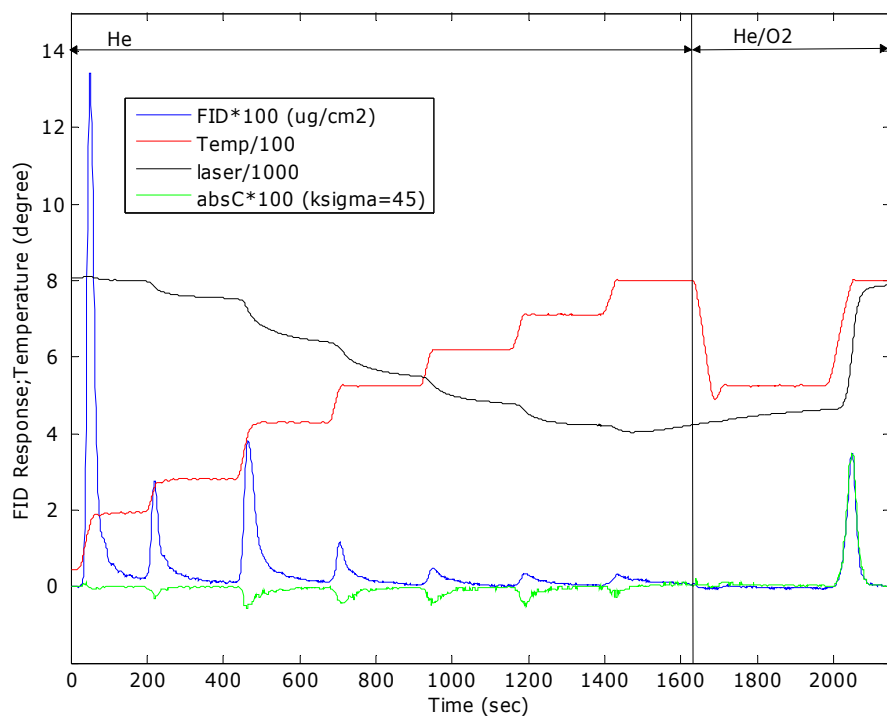
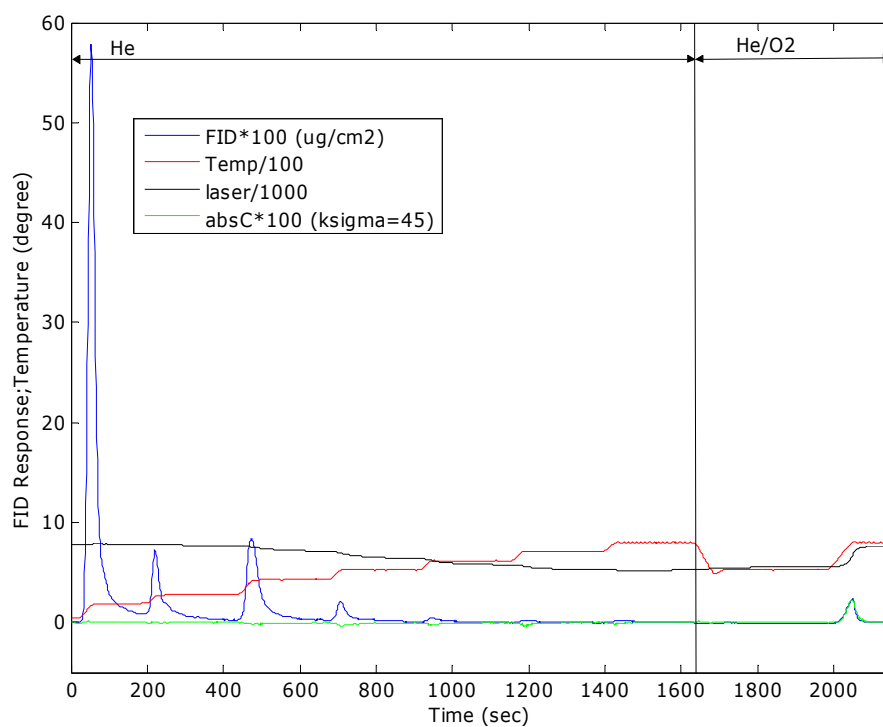


Fig 3b



3.1.3 Maximum He-mode Temperature and Organic Carbon

Lowering the temperature of the peak He-mode from 850°C certainly improves the accuracy of OC/EC split by avoiding the premature evolution of light-absorbing carbon. The major concern is however that, by lowering this temperature set point, OC might not all volatilize or completely pyrolyse during the He-mode of the analysis and slip into the He/O₂-mode instead. Under this circumstance, there would be the uncontrolled risk that a fraction of OC evolves even after the OC/EC split point and is then erroneously measured as native EC. To minimise the potential of this positive bias, we determine which temperature, lower than 850°C, would lead, in the He-mode, to a total volatilization or pyrolysis of OC. We analysed, therefore, quartz filters loaded with i) secondary organic aerosol (SOA), both anthropogenic and biogenic, ii) levoglucosan and iii) fulvic acid. The selected species represent some of the major components of the organic carbon aerosol fraction and the filters analysed do not contain EC. The protocol used for these tests is a *modified* EUSAAR_1 protocol; steps He-4 at 550°C, He-6 at 750°C and He-7 at 850°C were added, each of 240 s. Thermograms of these analyses are shown in **Figure 3**. The derivative of the laser transmission is used to trace the formation or release of light-absorbing carbon during the analysis and is visualised in the thermogram as negative carbon in the He-mode and positive carbon in the He/O₂-mode, respectively. Dividing the derivative by an appropriate specific cross section provides an estimate of the absorbing carbon formed or lost which complements standard thermal-optical analysis outputs (Bond, personal communication, 2007). Thermograms clearly show that a He-mode temperature $\leq 550^\circ\text{C}$, as a maximum, does not make all organic carbon evolve or completely pyrolyse in the He-mode. Organic carbon still evolves and chars at temperatures higher than 550°C. Let us now consider adding the selected organic species to real atmospheric aerosol samples, and obtain a mixture of OC species and EC. Our findings imply that thermal-optical analysis of these samples using a He4-550 protocol would result in a large fraction of organic carbon evolving in the He/O₂-mode, and potentially even after the OC/EC split point. If so, TOT-EC defined by a He-550 protocol, as IMPROVE, overestimates the native EC as compared to the one defined by protocols with higher temperatures for He4 step. To prevent this potential positive bias, it is advisable to increase the maximum He-mode temperature from 550°C; intermediate temperatures, however lower than 850°C, appear more adequate.

Figure 3a shows that a large fraction (91%) of the anthropogenic SOA carbon evolves and/or pyrolyses by the end of the 650°C step and even a larger fraction (96%) by the 750°C step completion. The results for biogenic SOA and levoglucosan (**Figure 3b** and **Figure 3c**) are quite similar: 98% of the carbon evolves and/or pyrolyses as the analysis completed the step at 650°C. Conversely, thermal-optical analysis of fulvic acid-spiked filters (**Figure 3d**) poses severe problems. Only ca. 80% of the carbon from fulvic acid evolves and/or pyrolyses by the end of the 650°C step, and at this point of the analysis, C is still evolving with a significant rate -i.e. the FID response is far from zero. Thus, in a He4-650 protocol, the remaining fraction of fulvic acid would carry over into He/O₂-mode. On the other hand, carrying out the analysis to temperature $\geq 650^\circ\text{C}$ leads to a significant release of pyrolysed carbon (See thermogram 3d). At the end of the 750 °C step, any estimate of the carbon fraction evolved and/or pyrolysed is impossible, being the carbon peak the sum of OC and prematurely evolved PC.

Fig 3c

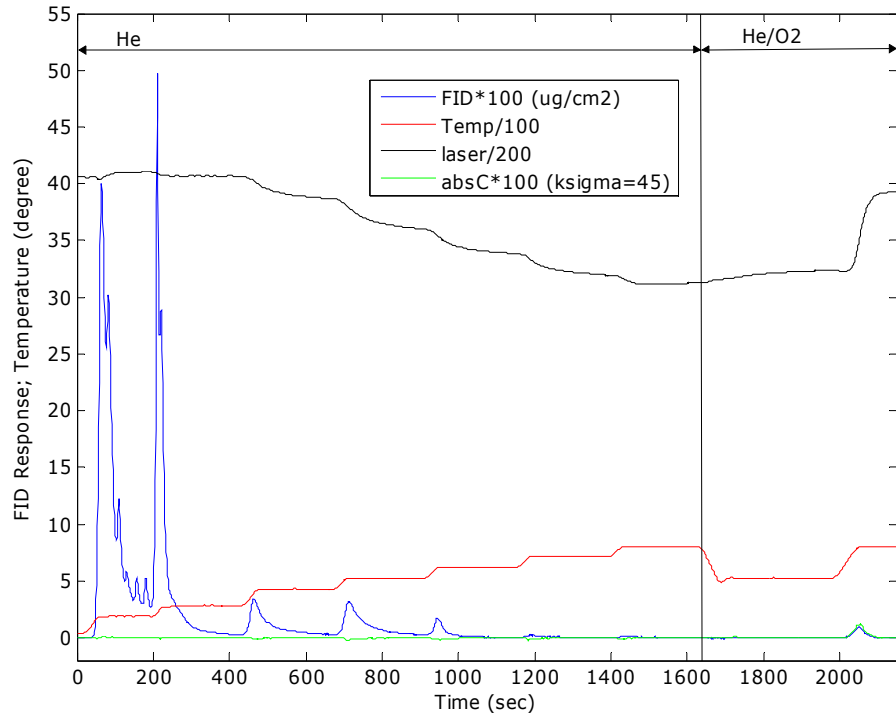
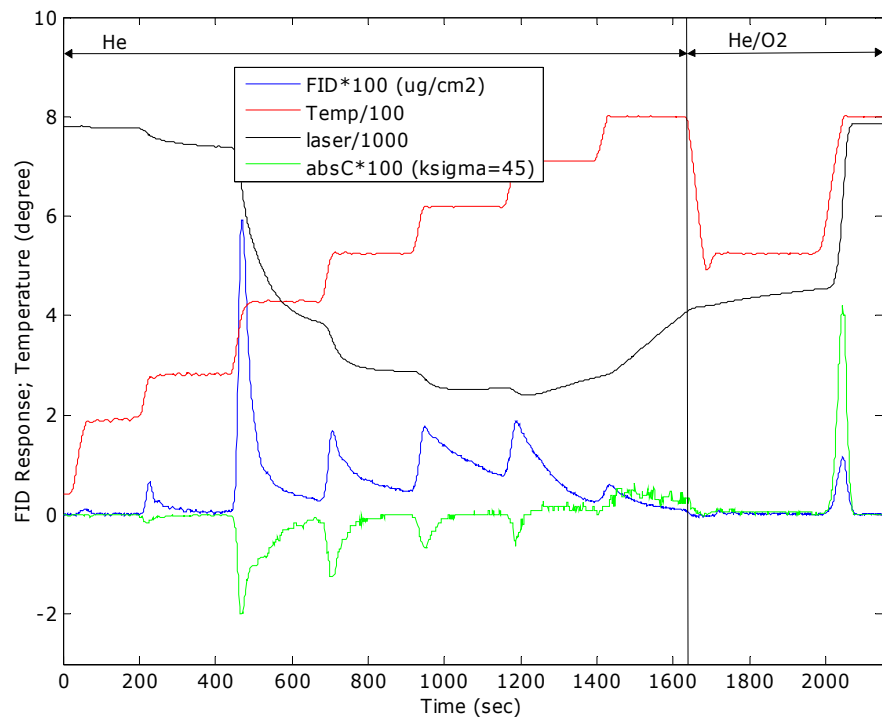


Fig 3d



Future work should be devoted to investigate the effect of prolonging the duration of the 650°C step. For atmospheric aerosol samples rich in such macromolecular organic carbon species, a longer residence time at He4-650 °C could promote a larger fraction of carbon driving off in the He-mode without an apparent concurrent loss of PC. This would reduce, in turn, the amount of organic carbon slipping into the He/O₂-mode and the magnitude of a potential positive bias of the post split EC.

Similar experiments were performed with PM_{2.5} atmospheric aerosol. Results confirmed that, for most samples, the FID response (evolved C) approaches the baseline and laser slope is zero at the 650°C step, and no significant organic carbon further evolves or chars at higher temperatures.

3.2 Temperature plateau durations

As reported in [Table 1](#), the NIOSH and IMPROVE protocols differ in the residence time at each temperature step. Typically, residence times are overall longer for IMPROVE than for NIOSH analysis. The IMPROVE residence times are variable, since the shifting to the next temperature set-point is not initiated until the slope of the FID response reaches zero. IMPROVE total analysis times are therefore quite long. On the contrary, NIOSH protocols explicitly fix the residence times at each temperature set-point, often giving rise to overlapping in OC peaks. In the literature, various residence times for NIOSH protocols are reported (e.g. Birch and Cary, 1996; Birch, 1998), depending on the nature of the analysed samples.

In this work, residence times at each temperature set-point have been explicitly specified so that i) FID response approaches the baseline before the next set-point; and ii) the total analysis time (including CH₄ standardisation) results acceptable for routine monitoring applications. Particularly crucial is the residence time of the highest He temperature step (650°C) which should guarantee that both the laser light transmission slope and the FID response equal zero, indicating no further pyrolysis and no OC left behind, respectively. Similarly, the duration of the highest temperature step (850°C) in He/O₂ should be sufficient to allow light-absorbing carbon species (PC and EC) to completely evolve before calibration, avoiding that left-behind LAC will slip into the methane calibration peak and bias both the total LAC load and the calibration peak.

Initially the residence times at each temperature step were defined according to the typical features of Ispra PM_{2.5} carbonaceous aerosol thermograms (EUSAAR_1 long). However, among the EUSAAR Supersites, Ispra certainly represents the site encountering the highest aerosol carbon concentration especially in wintertime. Analysis of Ispra summertime aerosol samples and of other background sites samples were performed in order to adjust the previously defined residence times to lower carbon contents satisfying, however, the requirements mentioned above. A shorter version of the EUSAAR_1 protocol was thus defined, EUSAAR_1 short ([Table 1](#)).

3.3 The Helium/Oxygen-Mode

Several tests were performed varying temperature and residence time to define steps in the He/O₂-mode. Ideally, OC/EC split should occur where the FID signal is low so that the uncertainty in the split point position results in a minimum uncertainty in the determination of the OC and EC amounts. On the basis of the analysis of atmospheric aerosol sampled in Ispra, two temperature steps were initially selected in the He/O₂-mode, specifically at 550°C and 850°C (EUSAAR_1 protocol).

However, validation analysis carried out on selected PM_{2.5} and PM₁₀ aerosol samples collected at various EUSAAR sites (e.g Birkenes in Norway) often showed a split point at the maximum of a high carbon peak. Further studies were performed to refine the temperature protocol in the He/O₂-mode. We concluded that the addition of a lower temperature step at 500°C and of an intermediate step at 700°C gives a smoother FID response profiles over the entire He/O₂-mode and thus leads to a lower uncertainty in the OC/EC split determination. A slightly revised thermal protocol-optical, namely EUSAAR_2, was thus defined ([Table 3](#)).

Table 3 EUSAAR_2 protocol: temperature set point and residence time are reported.

STEP	T, duration
He1	200°C, 120s
He2	300°C, 150s
He3	450°C, 180s
He4	650°C, 180s
(Helium)	Cool down, 30s
He/O ₂ 1 ^a	500°C, 120s
He/O ₂ 2 ^a	550°C, 120s
He/O ₂ 3 ^a	700°C, 70s
He/O ₂ 4 ^a	850°C, 80s

^a A mix of 1% oxygen in UHP helium

4 CONCLUSIONS

An accurate work has been performed to assess and then mitigate the effects of *events* occurring during the analysis that can potentially magnify the inherent biases affecting thermal-optical analyses of OC and EC. Our approach to improve the accuracy of the thermal-optical discrimination between OC and EC was essentially based on four goals. First, as charring correction relies on assumptions that proved to be generally not true, we sought to reduce pyrolysis to minimum levels in favor of a maximum volatilisation of organic carbon by adding and prolonging steps at lower temperature. Second, we sought to minimize the potential (negative) bias in EC determination, caused by early release of light absorbing species including native EC at high temperature in the He-mode. Third, we sought to minimize the potential positive bias in EC determination resulting from the slipping of residual organic carbon into the He/O₂-mode and its potential evolution after the split point by maximizing the evolution and/or charring of OC at high temperature in the He-mode. Finally, we sought to reduce the uncertainty arising from the position of the OC/EC split point on the FID profile through multiple desorption steps in the He/O₂-mode. In general, the present study demonstrates that the temperature protocol influences the relative biases possibly created by either premature evolution of light-absorbing material (EC or EC and PC), which is more marked at higher temperature, or slipping of non-light-absorbing carbon (OC) in the He/O₂-mode, that is enhanced at lower maximum He-mode temperature. When selecting a temperature protocol, one seeks to balance these two competing effects. Since both premature light absorbing carbon evolution and slipping of non-light absorbing carbon into the He/O₂-mode likely occur over a range of temperature and at various extents depending on sample load and composition, specifying a single thermal protocol at which both biases would disappear is impossible.

This work focused largely on the selection of the crucial highest He-mode temperature. Analyses of ambient aerosol samples and of light-absorbing-carbon-only samples were used to demonstrate that high temperatures in He (850°C) lead to premature LAC evolution. Thus, in atmospheric samples, the premature evolution in the He-mode of EC or of a combination of PC and EC lead the EC defined by a He4-850 protocol to be biased low because the specific cross section of PC was shown higher than that of EC. While this problem can be avoided by lowering the maximum He-mode temperature, analyses of ambient aerosol samples and various organics-spiked filters indicate that a too low maximum He-mode temperature ($\leq 550^\circ\text{C}$) allow non-light-absorbing carbon to slip into the He/O₂ mode of the analysis. If this carbon evolves after the OC/EC split, it biases the EC values high. Among the various protocols considered here, the protocol with the highest temperature step in He at 650 °C appeared to yield the best compromise between positive and negative biases and the most accurate estimation of EC in Ispra PM_{2.5} samples. Additional studies were carried out involving aerosol samples collected within the EUSAAR community -in particular Birkenes-Norway, K-puszt-Hungary and Montseny-Spain and i.e. affected by varying PM source emissions with different aging and load conditions; these studies allowed to a more comprehensive understanding of the thermal-optical behaviour of carbonaceous aerosol during analyses. Results confirmed that conditions as a maximum temperature in He-mode of 650°C and a multiple steps He/O₂ mode effectively minimize potential biases and finally led to a fine-tuned EUSAAR_2 protocol appropriate for different types of carbonaceous PM encountered across Europe.

Acknowledgments. We would like to acknowledge the support of the European Community – Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme, EUSAAR Contract N° RII3-CT-2006-026140. We also thank everyone involved in the planning and operation of these experiments.

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European Commission

EUR 23441 EN– Joint Research Centre – Institute for Environment and Sustainability

Title: Toward a Standardized Thermal-Optical Protocol for Measuring Atmospheric Organic and Elemental Carbon: The EUSAAR protocol

Author(s): Fabrizia Cavalli and Jean-Philippe Putaud

Luxembourg: Office for Official Publications of the European Communities

EUR – Scientific and Technical Research series – ISSN 1018-5593

ISBN 978-92-79-09561-0

DOI 10.2788/87062

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